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<b>(54) Title:</b> SUPPORTED POLYMERIZATION CATALYST		
<b>(57) Abstract</b>  An olefin polymerization catalyst comprising (a) a supported transition metal containing component comprising the support treated with at least one metallocene and at least one non-metallocene transition metal compound, and a cocatalyst comprising an alumoxane and an organometallic compound of a metal of Groups IA, IIA, IIB, or IIIA of the Periodic Table.		

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## SUPPORTED POLYMERIZATION CATALYST

1           This invention relates to a transition metal containing sup-  
2   ported catalyst component useful in combination with a cocatalyst for  
3   the polymerization and copolymerization of olefins and particularly  
4   useful for the polymerization of ethylene and copolymerization of  
5   ethylene with 1-olefins having 3 or more carbon atoms such as, for  
6   example, propylene, i-butene, 1-butene, 1-pentene, 1-hexene, 1-octene,  
7   cyclic olefins such as norbornene, and dienes such as butadiene,  
8   1,7-octadiene and 1,4-hexadiene. The invention further relates to a  
9   heterogeneous catalyst system comprising the transition metal contain-  
10   ing supported catalyst component and as a cocatalyst, the combination  
11   of an organometallic compound of a metal selected from Groups IA, IIA,  
12   IIB, and IIIA of the Periodic Table (66th Edition of Handbook of  
13   Chemistry of Physics, CRC Press, 1985-1986, CAS version) and an alum-  
14   oxane. The invention further generally relates to a process for poly-  
15   merization of ethylene alone or with other 1-olefins or diolefins in  
16   the presence of a catalyst system comprising the supported transition  
17   metal-containing catalyst component and an alumoxane.

18   Description of the Prior Art

19           Traditionally, ethylene and 1-olefins have been polymerized  
20   or copolymerized in the presence of hydrocarbon insoluble catalyst  
21   systems comprising a transition metal compound and an aluminum alkyl.  
22   More recently, active homogeneous catalyst systems comprising a bis-  
23   (cyclopentadienyl)titanium dialkyl or a bis(cyclopentadienyl)-zir-  
24   conium dialkyl, an aluminum trialkyl and water have been found to be  
25   useful for the polymerization of ethylene.

26           German Patent No. 2,608,863 discloses the use of a catalyst  
27   system for the polymerization of ethylene consisting of bis  
28   (cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water.

29           German Patent No. 2,608,933 discloses an ethylene  
30   polymerization catalyst system consisting of zirconium metallocenes of  
31   the general formula  $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$ , wherein n stands  
32   for a number in the range of 1 to 4, Y for R,  $\text{CH}_2\text{AlR}_2$ ,  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  
33    $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ , wherein R stands for alkyl or metallo alkyl, and an  
34   aluminum trialkyl cocatalyst and water.

35           European Patent No. 0035242 discloses a process for preparing  
36   ethylene polymers and atactic propylene polymers in the presence of a

1 halogen-free Ziegler catalyst system comprising (1) a cyclopentadienyl  
2 compound of the formula  $(\text{cyclopentadienyl})_n \text{MeY}_{4-n}$  in which n is an  
3 integer from 1 to 4, Me is a transition metal, especially zirconium,  
4 and Y is either hydrogen, a  $\text{C}_1\text{-C}_5$  alkyl or metallo alkyl group or  
5 a radical having the following general formula  
6  $\text{CH}_2\text{AlR}_2$ ,  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  $\text{CH}_2\text{CH}(\text{AlR}_2)_2$  in which R represents a  
7  $\text{C}_1\text{-C}_5$  alkyl or metallo alkyl group, and (2) an alumoxane.

8 Additional teachings of homogeneous catalyst systems compris-  
9 ing a metallocene and alumoxane are European Patent No. 0069951 of  
10 Kaminsky et al, and U.S. 4,404,344 issued September 13, 1983 of Sinn  
11 et al.

12 In "Molecular Weight Distribution and Stereoregularity Of  
13 Polypropylenes Obtained With  $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_3$  Catalyst System";  
14 Polymer, Pg. 469-471, 1981, Vol. 22, April, Doi, et al disclose pro-  
15 pylene polymerization with a catalyst which at about 41°C obtains a  
16 soluble catalyst and insoluble catalyst fraction, one with "homoge-  
17 neous catalytic centers" and the other with "heterogeneous catalytic  
18 centers". The polymerization at that temperature obtains polypropyl-  
19 ene having a bimodal molecular weight distribution.

20 An advantage of the metallocene-alumoxane homogeneous cata-  
21 lyst system is the very high activity obtained for ethylene polymeri-  
22 zation. Nevertheless, the catalysts suffer from a disadvantage, that  
23 is, the ratio of alumoxane to metallocene is high, for example, in the  
24 order of 1,000 to 1 or greater. Such voluminous amounts of alumoxane  
25 would require extensive treatment of polymer product obtained in order  
26 to remove the undesirable aluminum. Another disadvantage of the homo-  
27 geneous catalyst system is that the polymer product produced therefrom  
28 manifests small particle size and low bulk density.

29 In U. S. Patent 4,530,914, a homogeneous catalyst system  
30 comprising two different metallocenes for use in producing polyolefins  
31 having a broad molecular weight distri- bution and/or multi-modal  
32 molecular weight distribution is described.

33 In copending application USSN 697,308, filed February 1,  
34 1985, there is described a homogeneous catalyst system comprising two  
35 or more metallocenes, each having different reactivity ratios, for use  
36 in producing reactor blends, i.e., blends of two or more polymers

1 having a varied compositional distribution produced simultaneously in  
2 one reactor. Other teachings are found in U.S. Patent 4,522,982 and  
3 copending application 728,111, filed April 29, 1985.

4 James C. W. Chien, in "Reduction of Ti(IV) Alkyls in  
5 Cab-O-Sils Surfaces", Journal. of Catalysis 23, 71(1971); Dag  
6 Slotfeldt-Ellingsene et al. in "Heterogenization of Homogeneous  
7 Catalysts", Journal. Molecular Catalysis, 9, 423 (1980) disclose a  
8 supported titanocene in combination with alkyl aluminum halides as  
9 poor catalysts for olefin polymerization.

10 In copending application SN 747,616 filed June 21, 1985 a  
11 heterogeneous catalyst system comprising a supported metallocene and  
12 an alumoxane cocatalyst is disclosed.

13 It would be highly desirable to provide a metallocene based  
14 catalyst which is commercially useful for the polymerization of  
15 olefins wherein the aluminum to transition metal ratio is reduced  
16 compared with the known homogeneous systems, to provide a polymeri-  
17 zation catalyst system which produces polymer product having improved  
18 particle size and bulk density, and to provide a catalyst system which  
19 evidences improved comonomer incorporation in the production of, for  
20 example, linear low density polyethylene (LLDPE). It is particularly  
21 desirable to provide a catalyst system capable of producing polymers  
22 having a varied range of molecular weight distributions and/or compo-  
23 sitional distributions.

#### 24 Summary of the Invention

25 In accordance with the present invention, a catalyst system  
26 comprising (i) a metallocene and a non-metallocene transition metal  
27 compound (i.e. a transition metal compound not containing the cyclo-  
28 pentadienyl ring) supported catalyst component and (ii) a combination  
29 of an organometallic compound of a metal of Groups IA, IIA, IIB and  
30 IIIA of the Periodic Table and an alumoxane cocatalyst is provided for  
31 olefin polymerization, and particularly for the production of linear  
32 low, medium and high density polyethylenes and copolymers of ethylene  
33 with alpha-olefins having 3 or more carbon atoms ( $C_3-C_{18}$ ), cyclic  
34 olefins, and/or diolefins having up to 18 carbon atoms.

35 The supported catalyst component provided in accordance with  
36 one embodiment of this invention, comprises the product obtained by  
37 contacting at least one metallocene and at least one non-cyclopenta-  
38 dienyl transition metal compound and a support material thereby

1 providing a supported (multi)metallocene-non-metallocene transition  
2 metal compound olefin polymerization catalyst component.

3 In accordance with another embodiment of the invention, a  
4 catalyst system comprising a supported (multi) metallocene-noncyclo-  
5 pentadienyl transition metal compound and an organometallic compound  
6 alumoxane is provided which will polymerize olefins at commercially  
7 respectable rates without an objectionable excess of alumoxane as  
8 required in the homogenous system.

9 In yet another embodiment of this invention there is provided  
10 a process for the polymerization of ethylene and other olefins, and  
11 particularly homopolymers of ethylene and copolymers of ethylene and  
12 alpha-olefins and/or diolefins in the presence of the new catalyst  
13 system. The process, by means of the catalyst, provides the capabi-  
14 lity of producing polymers having a varied range of molecular weight  
15 distributions, i.e., from narrow molecular weight distribution to a  
16 broad molecular weight distribution and/or multi-modal molecular  
17 weight distribution. The process also provides the capability of  
18 producing reactor blends of polyethylene with polyethylene copolymers  
19 of selected composition.

20 The metallocenes employed in the production of the supported  
21 catalyst component are organometallic coordination compounds which are  
22 cyclopentadienyl derivatives of a Group IVB and VB metal of the  
23 Periodic Table and include mono, di and tricyclopentadienyls and their  
24 derivatives of the transition metals. Particularly desirable are the  
25 metallocenes of Group IVB metals such as titanium and zirconium.

26 The transition metal compounds employed in the production of  
27 the supported catalyst component are coordination compounds of a Group  
28 IVB, VB, or VIB metal, excluding cyclopentadienyl derivatives, but  
29 including the halide, alkoxide, oxyhalide, and hydride derivatives of  
30 the transition metals. Particularly desirable are the derivatives of  
31 Group IVB and VB metals such as titanium, zirconium, and vanadium.

32 The alumoxanes employed as the one component of the cocata-  
33 lyst system are themselves the reaction products of an aluminum tri-  
34 alkyl with water.

35 The alumoxanes are well known in the art and comprise oligo-  
36 meric, linear and/or cyclic alkyl alumoxanes represented by the for-  
37 mulae:

1 (I)  $R-(Al-O)_n-AlR_2$  for oligomeric, linear alumoxanes, and

2 R

3 (II)  $(-Al-O-)_m$  for oligomeric, cyclic alumoxanes,

4 R

5 wherein n is 1-40, preferably 1-20, m is 3-40, preferably 3-20 and R  
6 is a  $C_1-C_8$  alkyl group and preferably methyl. Generally, in the  
7 preparation of alumoxanes from, for example, trimethylaluminum and  
8 water, a mixture of linear and cyclic compounds is obtained.

9 The alumoxanes can be prepared in a variety of ways. Prefer-  
10 ably, they are prepared by contacting water with a solution of alumi-  
11 num trialkyl, such as, for example, trimethylaluminum, in a suitable  
12 organic solvent such as benzene or an aliphatic hydrocarbon. For  
13 example, the aluminum alkyl is treated with water in the form of a  
14 moist solvent. In a preferred method, the aluminum alkyl, such as  
15 trimethylaluminum, can be desirably contacted with a hydrated salt  
16 such as hydrated ferrous sulfate. The method comprises treating a  
17 dilute solution of trimethylaluminum in, for example, toluene with  
18 ferrous sulfate heptahydrate.

19 PREFERRED EMBODIMENTS

20 Briefly, the supported (multi) transition metal containing  
21 catalyst component of the present invention is obtained by contacting  
22 at least one metallocene and at least one non-cyclopentadienyl transi-  
23 tion metal compound (hereinafter "transition metal compound") with a  
24 solid porous support material. The supported product is employed as  
25 the transition metal-containing catalyst component for the polymeri-  
26 zation of olefins

27 Typically, the support can be any solid, particularly porous  
28 supports such as talc or inorganic oxides, or resinous support  
29 materials such as a polyolefin. Preferably, the support material is  
30 an inorganic oxide in finely divided form.

31 Suitable inorganic oxide materials which are desirably  
32 employed in accordance with this invention include Group IIA, IIIA,  
33 IVA or IVB metal oxides such as silica, alumina, and silica-alumina

1 and mixtures thereof. Other inorganic oxides that may be employed  
2 either alone or in combination with the silica, alumina or silica-  
3 alumina are magnesia, titania, zirconia, and the like. Other suitable  
4 support materials, however, can be employed, for example, finely  
5 divided polyolefins such as finely divided polyethylene.

6 The metal oxides generally contain acidic surface hydroxyl  
7 groups which will react with the metallocene added to the reaction  
8 slurry. Prior to use, the inorganic oxide support is dehydrated,  
9 i. e., subjected to a thermal treatment in order to remove water and  
10 reduce the concentration of the surface hydroxyl groups. The treat-  
11 ment is carried out in vacuum or while purging with a dry inert gas  
12 such as nitrogen at a temperature of about 100°C to about 1000°C, and  
13 preferably, from about 300°C to about 800°C. Pressure considerations  
14 are not critical. The duration of the thermal treatment can be from  
15 about 1 to about 24 hours; however, shorter or longer times can be  
16 employed provided equilibrium is established with the surface hydroxyl  
17 groups.

18 Chemical dehydration as an alternative method of dehydration  
19 of the metal oxide support material can advantageously be employed.  
20 Chemical dehydration converts all water and hydroxyl groups on the  
21 oxide surface to inert species. Useful chemical agents are for  
22 example,  $\text{SiCl}_4$ ; chlorosilanes, such as trimethylchlorosilane,  
23 dimethylaminotrimethylsilane and the like. The chemical dehydration is  
24 accomplished by slurrying the inorganic particulate material, such as,  
25 for example, silica in an inert low boiling hydrocarbon, such as, for  
26 example, hexane. During the chemical dehydration reaction, the silica  
27 should be maintained in a moisture and oxygen-free atmosphere. To the  
28 silica slurry is then added a low boiling inert hydrocarbon solution  
29 of the chemical dehydrating agent, such as, for example, dichlorodi-  
30 methylsilane. The solution is added slowly to the slurry. The  
31 temperature ranges during chemical dehydration reaction can be from  
32 about 25°C to about 120°C, however, higher and lower temperatures can  
33 be employed. Preferably, the temperature will be about 50°C to about  
34 70°C. The chemical dehydration procedure should be allowed to proceed  
35 until all the moisture is removed from the particulate support  
36 material, as indicated by cessation of gas evolution. Normally, the  
37 chemical dehydration reaction will be allowed to proceed from about 30



1 minutes to about 16 hours, preferably 1 to 5 hours. Upon completion  
2 of the chemical dehydration, the solid particulate material is  
3 filtered under a nitrogen atmosphere and washed one or more times  
4 with a dry, oxygen-free inert hydrocarbon solvent. The wash solvents,  
5 as well as the diluents employed to form the slurry and the solution  
6 of chemical dehydrating agent, can be any suitable inert hydrocarbon.  
7 Illustrative of such hydrocarbons are heptane, hexane, toluene, iso-  
8 pentane and the like.

9 The normally hydrocarbon soluble metallocene is converted to  
10 a heterogeneous supported catalyst by simply depositing said at least  
11 one metallocene on the support material.

12 Any of the conventional Ziegler-Natta transition metal  
13 compounds can be usefully employed as the transition metal component  
14 in preparing the supported catalyst component. Typically, the transi-  
15 tion metal component is a compound of a Group IVB, VB, or VIB metal.  
16 The transition metal component is generally represented by the for-  
17 mulas:  $\text{TrX}'_{4-q}(\text{OR}')_q$ ,  $\text{TrX}'_{4-q}\text{R}^2_q$ ,  $\text{VOX}'_3$  and  $\text{VO}(\text{OR}')_3$ .  
18 Tr is a Group IVB, VB, or VIB metal, preferably a Group IVB or VB  
19 metal and preferably titanium, vanadium or zirconium, q is 0 or a  
20 number equal to or less than 4, X' is a halogen and R<sup>1</sup> is an alkyl  
21 group, aryl group or cycloalkyl group having from 1 to 20 carbon  
22 atoms, and R<sup>2</sup> is an alkyl group, aryl group, aralkyl group, substi-  
23 tuted aralkyl group, and the like. The aryl, aralkyls and substituted  
24 aralkyls contain from 1 to 20 carbon atoms preferably 1 to 10 carbon  
25 atoms. When the transition metal compound contains a hydrocarbyl  
26 group, R<sup>2</sup>, being an alkyl, cycloalkyl, aryl, or aralkyl group, the  
27 hydrocarbyl group will preferably not contain an H atom in the posi-  
28 tion beta to the metalcarbon bond. Illustrative, but non-limiting  
29 examples of alkyl groups are methyl, neo-pentyl, 2,2-dimethylbutyl,  
30 2,2-dimethylhexyl; aryl groups such as phenyl, naphthyl; aralkyl  
31 groups such as benzyl; cycloalkyl groups such as 1-norbornyl.  
32 Mixtures of these transition metal compounds can be employed if  
33 desired.

34 Illustrative examples of the transition metal compounds  
35 include  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$ ,  
36  $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$ ,  $\text{Ti}(\text{OC}_6\text{H}_{13})_2\text{Cl}_2$ ,  $\text{Ti}(\text{OC}_8\text{H}_{17})_2\text{Br}_2$  and

1  $Ti(OC_{12}H_{25})Cl_3$ . Illustrative examples of vanadium compounds include  
 2  $VCl_4$ ,  $VOC_2H_5$ ,  $VO(OC_2H_5)_3$ , and  $VO(OC_4H_9)_3$ . Illustrative examples  
 3 of zirconium compounds include  $ZrCl_4$ ,  $ZrCl_3(OC_2H_5)$ ,  
 4  $ZrCl_2(OC_2H_5)_2$ ,  $ZrCl(OC_2H_5)_3$ ,  $Zr(OC_2H_5)_4$ ,  $ZrCl_3(OC_4H_9)$ ,  
 5  $ZrCl_2(OC_4H_9)_2$ , and  $ZrCl(OC_4H_9)_3$ .

6 As indicated above, mixtures of the transition metal com-  
 7 pounds may be usefully employed, no restriction being imposed on the  
 8 number of transition metal compounds which may be contacted with the  
 9 support and one or more metallocenes. Any halogenide and alkoxide  
 10 transition metal compound or mixtures thereof can be usefully  
 11 employed. The previously named transition metal compounds are espe-  
 12 cially preferred with vanadium tetrachloride, vanadium oxychloride,  
 13 and titanium tetrachloride being most preferred.

14 The present invention employs at least one metallocene  
 15 compound in the formation of the supported catalyst. Metallocene,  
 16 i.e. a cyclopentadienide, is a metal derivative of a cyclopenta-  
 17 diene. The metallocenes usefully employed in accordance with this  
 18 invention contain at least one cyclopentadiene ring. The metal is  
 19 selected from Group IVB, or VB metals, preferably titanium, zirco-  
 20 nium, hafnium, and vanadium, and especially titanium and zirconium.  
 21 The cyclopentadienyl ring can be unsubstituted or contain substi-  
 22 tuents such as, for example, hydrocarbyl substituents. The metallo-  
 23 cene can contain one, two, or three cyclopentadienyl ring however two  
 24 rings are preferred.

25 The metallocenes can be represented by the general formulas:

26 I.  $(Cp)_m M R_n X_q$

27 wherein Cp is a cyclopentadienyl ring, M is a Group IVB, or VB tran-  
 28 sition metal, R is a hydride or a hydrocarbyl group having from 1 to  
 29 20 carbon atoms, X is a halogen atom, m = 1-3, n = 0-3, q = 0-3 and  
 30 the sum of m+n+q is equal to the oxidation state of M.

31 II.  $(C_5R'_k)_g R''_s (C_5R'_k)MQ_{3-g}$  and

32 III.  $R''_s (C_5R'_k)_2 MQ'$

33 wherein  $(C_5R'_k)$  is a cyclopentadienyl or substituted cyclopenta-  
 34 dienyl, each R' is the same or different and is hydrogen or a hydro-  
 35 carbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl  
 36 radical containing from 1 to 20 carbon atoms or two carbon atoms are  
 37 joined together to form a  $C_4-C_6$  ring, R'' is a  $C_1-C_4$  alkylene radical,  
 38 a dialkyl germanium or silicon, or a alkyl phosphine or amine

1 radical bridging two ( $C_5R'_k$ ) rings, Q is a hydrocarbyl radical  
2 such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having  
3 from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon  
4 atoms or halogen and can be the same or different from each other, Q'  
5 is an alkylidene radical having from 1 to about 20 carbon atoms, s is  
6 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1, and k  
7 is 5 when s is 0, and M is as defined above.

8 Exemplary hydrocarbyl radicals are methyl, ethyl, propyl,  
9 butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl,  
10 cetyl, 2-ethylhexyl, phenyl and the like.

11 Exemplary halogen atoms include chlorine, bromine, fluorine  
12 and iodine and of these halogen atoms, chlorine is preferred.

13 Exemplary hydrocarboxy radicals are methoxy ethoxy, butoxy,  
14 amyloxy and the like.

15 Exemplary of the alkylidene radicals is methylenidene, ethy-  
16 lenidene and propylenidene.

17 Illustrative, but non-limiting examples of the metallocenes  
18 represented by formula I are dialkyl metallocenes such as bis(cyclo-  
19 pentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl,  
20 bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)-zir-  
21 conium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl,  
22 bis(cyclopentadienyl)titanium dineopentyl, bis(cyclopentadienyl)-  
23 zirconium dineopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis-  
24 (cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium  
25 dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)-  
26 titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl  
27 chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclo-  
28 pentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium  
29 ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis-  
30 (cyclopentadienyl)titanium methyl bromide, bis(cyclopentadienyl)-  
31 titanium methyl iodide, bis(cyclopentadienyl)titanium ethyl bromide,  
32 bis(cyclopentadienyl)titanium ethyl iodide, bis(cyclopentadienyl)-  
33 titanium phenyl bromide, bis(cyclopentadienyl)titanium phenyl iodide,  
34 bis(cyclopentadienyl)zirconium methyl bromide, bis(cyclopentadienyl)-  
35 zirconium methyl iodide, bis(cyclopentadienyl)zirconium ethyl bromide,  
36 bis(cyclopentadienyl)zirconium ethyl iodide, bis(cyclopentadienyl)-  
37 zirconium phenyl bromide, bis(cyclopentadienyl)zirconium phenyl  
38 iodide; the trialkyl metallocenes such as cyclopentadienyltitanium

1 trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl  
2 zirconium trineopentyl, cyclopentadienylzirconium trimethyl, cyclo-  
3 pentadienylhafnium triphenyl, cyclopentadienylhafnium trineopentyl,  
4 and cyclopentadienylhafnium trimethyl.

5 Illustrative, but non-limiting examples of II and III metal-  
6 locenes which can be usefully employed in accordance with this inven-  
7 tion are monocyclopentadienyls titanocenes such as, pentamethylcyclo-  
8 pentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium  
9 trichloride, bis(pentamethylcyclopentadienyl) titanium diphenyl, the  
10 carbene represented by the formula  $\text{Cp}_2\text{Ti}=\text{CH}_2$   
11 and derivatives of this reagent such as  $\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_3$ ,  
12  $(\text{Cp}_2\text{TiCH}_2)_2$ , and  $\text{Cp}_2\text{TiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ ,  $\text{Cp}_2\text{Ti}-\text{CH}_2\text{CH}_2\text{CH}_2$ ;  
13 substituted bis(Cp)Ti(IV) compounds such as bis(indenyl)titanium  
14 diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl  
15 or dihalides; dialkyl, trialkyl, tetra-alkyl and pentaalkyl cyclopen-  
16 tadienyl titanium compounds such as bis(1,2-dimethylcyclopenta-  
17 dienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopenta-  
18 dienyl)titanium diphenyl or dichloride and other dihalide complexes;  
19 silicon, phosphine, amine or carbon bridged cyclopentadiene  
20 complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl  
21 or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl  
22 or dichloride, methylenedicyclopentadienyl titanium diphenyl or  
23 dichloride and other dihalide complexes and the like.

24 Illustrative but non-limiting examples of the zirconocenes  
25 of Formula II and III which can be usefully employed in accordance  
26 with this invention are, pentamethylcyclopentadienyl zirconium tri-  
27 chloride, pentaethylcyclopentadienyl zirconium trichloride, the alkyl  
28 substituted cyclopentadienes, such as bis(ethylcyclopentadienyl)-  
29 zirconium dimethyl, bis( $\beta$ -phenylpropylcyclopentadienyl)zirconium  
30 dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, bis(n-butyl-  
31 cyclopentadienyl)zirconium dimethyl, bis(cyclohexylmethylcyclopenta-  
32 tadienyl)zirconium dimethyl, bis(n-octyl-cyclopentadienyl)- zirconium  
33 dimethyl, and haloalkyl and dihalide complexes of the above; dialkyl,  
34 trialkyl, tetra-alkyl, and pentaalkyl cyclopentadienes, such as bis-  
35 (pentamethylcyclopentadienyl)zirconium diphenyl, bis(pentamethyl-  
36 cyclopentadienyl)zirconium dimethyl, bis(1,2-dimethylcyclopenta-  
37 dienyl)zirconium dimethyl and mono- and dihalide complexes of the  
38 above; silicon, phosphorus, and carbon bridged cyclopentadiene

1 complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl,  
2 methyl halide or dihalide, and methylene dicyclopentadienyl zirconium  
3 dimethyl, methyl halide, or dihalide; carbenes represented by the  
4 formulae  $\text{Cp}_2\text{Zr}=\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$ , and derivatives of these compounds  
5 such as  $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ .

6 Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopenta-  
7 dienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium dichloride and  
8 the like are illustrative of other metallocenes.

9 The treatment of the support material, as mentioned above, is  
10 conducted in an inert solvent. The same inert solvent or a different  
11 inert solvent can also employed to dissolve the metallocenes and, if  
12 desired and/or required, the transition metal component. Preferred  
13 solvents include mineral oils and the various hydrocarbons which are  
14 liquid at reaction temperatures and in which the metallocenes are  
15 soluble. Illustrative examples of useful solvents include the alkanes  
16 such as pentane, iso-pentane, hexane, heptane, octane and nonane;  
17 cycloalkanes such as cyclopentane and cyclohexane; and aromatics such  
18 as benzene, toluene, ethylbenzene and diethylbenzene. Preferably the  
19 support material is slurried in toluene and the metallocene(s) is  
20 dissolved in toluene prior to addition to the support material. The  
21 one or more transition metal component(s) can be contacted with the  
22 support material together with the metallocene(s) by dissolving or  
23 slurrying in the solvent, it can be contacted separately and simulta-  
24 neously as a solution or neat with the support, or the transition  
25 metal component can be contacted prior to or subsequent to contacting  
26 the metallocene with the support material. The amount of solvent to  
27 be employed is not critical. Nevertheless, the amount employed should  
28 provide adequate heat transfer away from the catalyst components  
29 during reaction and permit good mixing.

30 The one or more metallocene(s) and the one or more transition  
31 metal component(s) can be added to the support material rapidly or  
32 slowly. The temperature maintained during the contact of the  
33 reactants can vary widely, such as, for example, from 0° to 100°C.  
34 Greater or lesser temperatures can also be employed. Preferably, the  
35 contacting of the at least one metallocene and the at least one  
36 transition metal compound with the silica is performed at room temper-  
37 ature. The reaction between the at least one metallocene and the  
38 support material is rapid, however, it is desirable that the at least

1 one metallocene be contacted with the support material for about one  
2 hour up to eighteen hours or greater. Preferably, the reaction is  
3 maintained for about one hour. The reaction of the at least one  
4 metallocene with the support material is evidenced by elemental ana-  
5 lysis of the support material for the transition metal contained in  
6 the metallocene(s).

7 At all times, the individual ingredients as well as the  
8 recovered catalyst component are protected from oxygen and moisture.  
9 Therefore, the contacting must be performed in an oxygen and moisture  
10 free atmosphere and recovered in an oxygen and moisture free atmo-  
11 sphere. Preferably, therefore, the contacting is performed in the  
12 presence of an inert dry gas such as, for example, nitrogen. The  
13 recovered solid catalyst is maintained in a nitrogen atmosphere.

14 Upon completion of the contacting of the at least one metal-  
15 locene and the at least one transition metal component with the  
16 support, the solid catalyst component can be recovered by any well-  
17 known technique. For example, the solid material can be recovered  
18 from the liquid by vacuum evaporation, filtration or decantation. The  
19 solid is thereafter dried by any suitable drying technique, such as,  
20 drying under a stream of pure dry nitrogen or drying under vacuum.

21 The total amount of metallocene usefully employed in prepa-  
22 ration of the solid supported catalyst component can vary over a wide  
23 range. The concentration of the metallocene deposited on the essen-  
24 tially dry support can be in the range of about 0.001 to about  
25 5 mmoles/g of support, however, greater or lesser amounts can be use-  
26 fully employed. Preferably, the metallocene concentration is in the  
27 range of 0.010 to 2 mmoles/g of support and especially 0.03 to  
28 1 mmoles/g of support.

29 The molar ratio of the metallocene component to the transi-  
30 tion metal component can vary over a wide range and in accordance with  
31 this invention is limited only by the breadth of the molecular weight  
32 distribution desired. The ratio can be in the range of about 100 to  
33 about 0.01 and preferably about 10 to about 0.1 moles metallocene  
34 component per mole of transition metal component.

35 It is highly desirable to have for many applications, such as  
36 extrusion and molding processes, polyethylenes which have a broad  
37 molecular weight distribution (BMWD) of the unimodal or the multi-  
38 modal type. Such polyethylenes evidence excellent processability,

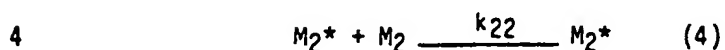
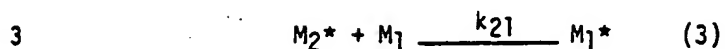
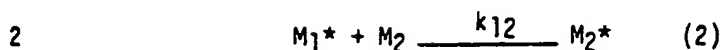
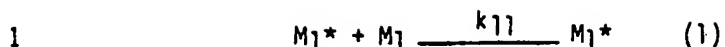
1 i.e., they can be processed at a faster throughput rate with lower  
2 energy requirements and at the same time such polymers would evidence  
3 reduced melt flow perturbations. The polyethylenes can be obtained by  
4 using the supported catalyst of this invention comprising the at least  
5 one metallocene and the at least one transition metal component. In  
6 accordance with the invention, BMWD polyethylenes can be obtained by  
7 employing on one support metallocenes and transition metal components  
8 which will have different propagation and termination rate constants  
9 for ethylene polymerization. Such rate constants are readily deter-  
10 mined by one of ordinary skill in the art.

11 The MWD of the polyethylenes can also readily be controlled  
12 by varying the molar ratios of the metallocene to transition metal  
13 component on the support. Conventional polymerization adjuvants such-  
14 as hydrogen, can be employed to control the molecular weight of the  
15 polymer produced.

16 The present invention also provides a process for producing  
17 (co)polyolefin reactor blends comprising polyethylene and copolyethyl-  
18 ene- $\alpha$ -olefins. The reactor blends are obtained directly during a  
19 single polymerization process, i.e., the blends of this invention are  
20 obtained in a single reactor by simultaneously polymerizing ethylene  
21 and copolymerizing ethylene with an  $\alpha$ -olefin thereby eliminating  
22 expensive blending operations. The process of producing reactor  
23 blends in accordance with this invention can be employed in con-  
24 junction with other prior art blending techniques, for example the  
25 reactor blends produced in a first reactor can be subjected to further  
26 blending in a second stage by use of the series reactors.

27 In order to produce reactor blends the supported metallo-  
28 cene-transition metal component catalyst comprises metallocenes and  
29 transition metal compounds having different reactivity ratios.

30 The reactivity ratios of the metallocenes and transition  
31 metal components in general are obtained by methods well known such  
32 as, for example, as described in "Linear Method for Determining  
33 Monomer Reactivity Ratios in Copolymerization", M. Fineman and S. D.  
34 Ross, J. Polymer Science 5, 259 (1950) or "Copolymerization", F. R.  
35 Mayo and C. Walling, Chem. Rev. 46, 191 (1950) incorporated herein in  
36 its entirety by reference. For example, to determine reactivity  
37 ratios the most widely used copolymerization model is based on the  
38 following equations:



5 where  $M_i$  refers to a monomer molecule which is arbitrarily design-  
6 nated  $i$  (where  $i = 1, 2$ ) and  $M_i^*$  refers to a growing polymer chain  
7 to which monomer  $i$  has most recently attached.

8 The  $k_{ij}$  values are the rate constants for the indicated  
9 reactions. In this case,  $k_{11}$  represents the rate at which an ethyl-  
10 ene unit inserts into a growing polymer chain in which the previously  
11 inserted monomer unit was also ethylene. The reactivity rates follow  
12 as:  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$  wherein  $k_{11}$ ,  $k_{12}$ ,  $k_{22}$   
13 and  $k_{21}$  are the rate constants for ethylene (1) or comonomer (2)  
14 addition to a catalyst site where the last polymerized monomer is  
15 ethylene ( $k_{1X}$ ) or comonomer (2) ( $k_{2X}$ ).

16 In Table I the ethylene-propylene reactivity ratios  $r_1$  and  
17  $r_2$  are listed for several metallocenes and transition metal compo-  
18 nents.

19 It can be seen from Table I that if one desires a blend  
20 comprising HDPE/ethylene-propylene copolymer one would select  
21  $(Me_5Cp)_2ZrCl_2$  and  $TiCl_4$  in ratios of about 1 to 10 to about 10  
22 to 1 whereas if one desires a blend comprising LLDPE/ethylene-  
23 propylene one would select  $(MeCp)_2ZrCl_2$  and  $VCl_4$  in ratios of  
24 about 1 to 10 to about 10 to 1.

25 Desirably, the molar ratio of metallocene to transition metal  
26 component on the support will be about 100 to 1 to about 1 to 100, and  
27 preferably 10 to 1 to about 1 to 10. The specific metallocenes  
28 selected and their molar ratios are dependent upon the molecular  
29 composition desired for the component polymers and the overall compo-  
30 sition desired for the blend. In general, the component catalyst used  
31 in a reactor blend catalyst mixture will each have  $r$  values which are  
32 different in order to produce final polymer compositions which  
33 comprise blends of two or more polymers.



TABLE I

	Catalyst	r <sub>1</sub>	r <sub>2</sub>
3	$\text{Cp}_2\text{Ti}=\text{CH}_2 \text{ Al}(\text{Me})_2\text{Cl}$	24	0.0085
4	$\text{Cp}_2\text{TiPh}_2$	19.5 $\pm$ 1.5	0.015 $\pm$ .002
5	$\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$	24 $\pm$ 2	0.029 $\pm$ .007
6	$\text{Cp}_2\text{ZrCl}_2$	48 $\pm$ 2	0.015 $\pm$ .003
7	$(\text{MeCp})_2\text{ZrCl}_2$	60	
8	$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$	250 $\pm$ 30	.002 $\pm$ 0.001
9	$[\text{Cp}_2\text{ZrCl}]_2\text{O}$	50	0.007
10	$\text{TiCl}_3$ (a)	15.7	0.110
11	$\text{TiCl}_4$ (a)	33.4	0.032
12	$\text{VCl}_3$ (a)	5.6	0.145
13	$\text{VCl}_4$ (a)	7.1	0.088
14	$\text{VO}(\text{OR})_x\text{Cl}_{3-x}$ (a)	17-28	--
15	$\text{ZrCl}_4$ (a)	61	--

(a) J. Boor, Ziegler-Natta Catalysts and Polymerizations, Academic Press, New York, 1979, P. 577.

The cocatalyst system employed in accordance with this invention comprises an alumoxane and an organic compound of a metal of Groups 1 through 3 of the Periodic Table.

Examples of the organic metal compounds employed in combination with the catalyst component are organic compounds of lithium, magnesium, calcium, zinc, and aluminum. Among other organic metal compounds just mentioned, organic aluminum compounds prove particularly desirable. The organic aluminum compounds usable herein are represented by the general formula  $\text{R}_n\text{AlX}_{3-n}$  (wherein R denotes an alkyl group or an aryl group having from 1-18 carbon atoms, X denotes a halogen atom, an alkoxy group or a hydrogen atom, and n denotes a desired number in the range of 1 to 3). Particularly desirable examples of the organic aluminum compounds are alkyl aluminum compounds such as trialkyl aluminum, dialkyl aluminum monohalide, monoalkyl aluminum dihalide, alkyl aluminum sesquihalide, dialkyl aluminum monoalkoxide, and dialkyl aluminum monohydride, respectively having 1 to 18 carbon atoms, preferably 2 to 6 carbon atoms, and mixtures and complex compounds thereof. Illustrative examples of such

1 organic aluminum compounds are trialkyl aluminums such as trimethyl  
 2 aluminum, triethyl aluminum, tripropyl aluminum, triisobutyl aluminum,  
 3 and trihexyl aluminum, dialkyl aluminum monohalides such as dimethyl  
 4 aluminum chloride, diethyl aluminum chloride, diethyl aluminum  
 5 bromide, diethyl aluminum iodide, and diisobutyl aluminum chloride,  
 6 monoalkyl aluminum dihalides such as methyl aluminum dichloride, ethyl  
 7 aluminum dichloride, methyl aluminum dibromide, ethyl aluminum  
 8 dibromide, ethyl aluminum diiodide, and isobutyl aluminum dichloride,  
 9 alkyl aluminum sesquihalides such as ethyl aluminum sesquichloride,  
 10 dialkyl aluminum monoalkoxides such as dimethyl aluminum methoxide,  
 11 diethyl aluminum ethoxide, diethyl aluminum phenoxide, dipropyl  
 12 aluminum ethoxide, diisobutyl aluminum ethoxide, and diisobutyl  
 13 aluminum phenoxide, and dialkyl aluminum hydrides such as dimethyl  
 14 aluminum hydride, diethyl aluminum hydride, dipropyl aluminum hydride,  
 15 and diisobutyl aluminum hydride. Among other organic aluminum  
 16 compounds enumerated above, trialkyl aluminums, specifically trimethyl  
 17 aluminum, triethyl aluminum, and triisobutyl aluminum, prove particu-  
 18 larly desirable. The trialkyl aluminum can be used in combination  
 19 with other organic aluminum compounds such as diethyl aluminum  
 20 chloride, ethyl aluminum dichloride, ethyl aluminum sesquichloride,  
 21 diethyl aluminum ethoxide, or diethyl aluminum hydride which are  
 22 available commercially. These other organic aluminum compounds may be  
 23 used in the form of a mixture or complex compound.

24 Further, an organic aluminum compound having two or more  
 25 aluminum atoms linked through the medium of an oxygen atom or nitrogen  
 26 atom is also usable. Concrete examples of this organic aluminum  
 27 compound are  $(C_2H_5)_2AlOAl(C_2H_5)_2$ ,  $(C_4H_9)_2AlOAl(C_4H_9)_2$ , and  
 28  $(C_2H_5)_2AlNA1(C_2H_5)_2$ .

29  $\begin{array}{c} | \\ C_2H_5 \end{array}$

30 Examples of organic compounds of metals other than aluminum  
 31 are diethyl magnesium, ethyl magnesium chloride, diethyl zinc and such  
 32 compounds as  $LiAl(C_2H_5)_4$  and  $LiAl(C_7H_{15})_4$ .

33 The ratio of alumoxane to the organometallic compound can  
 34 vary over a wide range and is generally controlled only by the ratio  
 35 of metallocene to transition metal component. The ratio of alumoxane  
 36 to metallocene can vary widely and is generally in the range of about  
 37 1 to 100 moles of aluminum per mole of metallocene metal on the

1 support. The ratio of organometallic compound to transition metal  
2 component will generally be in the range of about 1 to about 100 moles  
3 of aluminum per mole of transition metal component metal on the  
4 support. The alumoxane and the organometallic compound can be mixed  
5 in the desired ratio in a suitable hydrocarbon solvent and as isopen-  
6 tane, hexane, or toluene.

7 The inorganic oxide support used in the preparation of the  
8 catalyst may be any particulate oxide or mixed oxide as previously  
9 described which has been thermally or chemically dehydrated such that  
10 it is substantially free of adsorbed moisture.

11 The specific particle size, surface area, pore volume, and  
12 number of surface hydroxyl groups characteristic of the inorganic  
13 oxide are not critical to its utility in the practice of the inven-  
14 tion. However, since such characteristics determine the amount of  
15 inorganic oxide to be employed in preparing the catalyst compositions,  
16 as well as affecting the properties of polymers formed with the aid of  
17 the catalyst compositions, these characteristics must frequently be  
18 taken into consideration in choosing an inorganic oxide for use in a  
19 particular aspect of the invention. For example, when the catalyst  
20 composition is to be used in a gas-phase polymerization process - a  
21 type of process in which it is known that the polymer particle size  
22 can be varied by varying the particle size of the support - the inor-  
23 ganic oxide used in preparing the catalyst composition should be one  
24 having a particle size that is suitable for the production of a  
25 polymer having the desired particle size. In general, optimum results  
26 are usually obtained by the use of inorganic oxides having an average  
27 particle size in the range of about 30 to 600 microns, preferably  
28 about 30 to 100 microns; a surface area of about 50 to 1,000 square  
29 meters per gram, preferably about 100 to 400 square meters per gram;  
30 and a pore volume of about 0.5 to 3.5 cc per gram; preferably about  
31 0.5 to 2cc per gram.

32 The polymerization may be conducted by a solution, slurry, or  
33 gas-phase technique, generally at a temperature in the range of about  
34 0°-160°C or even higher, and under atmospheric, subatmospheric, or  
35 superatmospheric pressure conditions; and conventional polymerization  
36 adjuvants, such as hydrogen may be employed if desired. It is  
37 generally preferred to use the catalyst composition at a concentration  
38 such as to provide about 0.000001 - 0.005%, most preferably about

1 0.00001 - 0.0003%, by weight of transition metal based on the weight  
2 of monomer(s), in the polymerization of ethylene, alone or with one or  
3 more higher olefins.

4 A slurry polymerization process can utilize sub- or super-  
5 atmospheric pressures and temperatures in the range of 40-110°C. In a  
6 slurry polymerization, a suspension of solid, particulate polymer is  
7 formed in a liquid polymerization medium to which ethylene, alpha-  
8 olefin comonomer, hydrogen and catalyst are added. The liquid  
9 employed as the polymerization medium can be an alkane or cycloalkane,  
10 such as butane, pentane, hexane, or cyclohexane, or an aromatic hydro-  
11 carbon, such as toluene, ethylbenzene or xylene. The medium employed  
12 should be liquid under the conditions of the polymerization and rela-  
13 tively inert. Preferably, hexane or toluene is employed.

14 A gas-phase polymerization process utilizes superatmospheric  
15 pressure and temperatures in the range of about 50°-120°C. Gas-phase  
16 polymerization can be performed in a stirred or fluidized bed of cata-  
17 lyst and product particles in a pressure vessel adapted to permit the  
18 separation of product particles from unreacted gases. Thermostated  
19 ethylene, comonomer, hydrogen and an inert diluent gas such as nitro-  
20 gen can be introduced or recirculated so as to maintain the particles  
21 at a temperature of 50°-120°C. Polymer product can be withdrawn  
22 continuously or semi-continuously at a rate such as to maintain a  
23 constant product inventory in the reactor. After polymerization and  
24 deactivation of the catalyst, the product polymer can be recovered by  
25 any suitable means. In commercial practice, the polymer product can  
26 be recovered directly from the gas phase reactor, freed of residual  
27 monomer with a nitrogen purge, and used without further deactivation  
28 or catalyst removal. The polymer obtained can be extruded into water  
29 and cut into pellets or other suitable comminuted shapes. Pigments,  
30 anti-oxidants and other additives, as is known in the art, may be  
31 added to the polymer.

32 The molecular weight of polymer product obtained in accor-  
33 dance with this invention can vary over a wide range, such as low as  
34 500 up to 2,000,000 or higher and preferably 1,000 to about 500,000.

35 In order to further improve catalyst performance, surface  
36 modification of the support material may be desired. Surface  
37 modification is accomplished by specifically treating the support  
38 material such as silica, alumina or silica-alumina with an

1 organometallic compound having hydrolytic character. More.  
2 particularly, the surface modifying agents for the support materials  
3 comprise the organometallic compounds of the metals of Group IIA and  
4 IIIA of the Periodic Table. Most preferably the organometallic  
5 compounds are selected from magnesium and aluminum organometallics  
6 and especially from magnesium and aluminum alkyls or mixtures thereof  
7 represented by the formulas  $R^1MgR^2$  and  $R^1R^2AlR^3$  wherein each of  $R^1$ ,  
8  $R^2$  and  $R^3$  which may be the same or different are alkyl groups, aryl  
9 groups, cycloalkyl groups, aralkyl groups, alkoxide groups, alkenyl  
10 groups or alkenyl groups. The hydrocarbon groups  $R^1$ ,  $R^2$  and  $R^3$  can  
11 contain between 1 and 20 carbon atoms and preferably from 1 to about  
12 10 carbon atoms.

13 The surface modifying action is effected by adding the  
14 organometallic compound in a suitable solvent to a slurry of the  
15 support material. Contact of the organometallic compound in a suit-  
16 able solvent and the support is maintained from about 30 to 180  
17 minutes and preferably from 60 to 90 minutes at a temperature in the  
18 range of 20 to 100 °C. The diluent employed in slurrying the support  
19 can be any of the solvents employed in solubilizing the organome-  
20 tallic compound and is preferably the same.

21 The amount of surface modifying agent employed in prepa-  
22 ration of the surface modified support material can vary over a wide  
23 range. Generally the amount will be in the range of  $1 \times 10^{-6}$  moles  
24 to about  $2 \times 10^{-3}$  moles of modifying agent per gram of support  
25 material. However greater or lesser amounts can be employed.

26 Illustrative, but non-limiting examples of magnesium  
27 compounds which may be suitably employed as a surface modifying agent  
28 for the support materials in accordance with the invention are dialkyl  
29 magnesiums such as diethylmagnesium, dipropylmagnesiums, di-isopropyl-  
30 magnesium, di-n-butylmagnesium, di-isobutylmagnesium, diamylmagnesium,  
31 di-n-octylmagnesium, di-n-hexylmagnesium, di-n-decylmagnesium, and  
32 di-n-dodecylmagnesium; dicycloalkylmagnesiums, such as dicyclohexyl-  
33 magnesium; diarylmagnesiums such as dibenzylmagnesium, ditolylmag-  
34 nesium and dixylylmagnesium, alkylalkoxy magnesium such as ethyl  
35 magnesium ethoxide and the like.

36 Illustrative, but non-limiting examples of the aluminum  
37 compounds which may be suitably employed in accordance with the  
38 invention are trialkylaluminums such as trimethylaluminum, triethyl-

1 aluminum, tripropylaluminum, tri-isobutylaluminum, tri-n-hexylalu-  
 2 minum, and tri-n-octylaluminum. Preferably, the organoaluminum  
 3 compounds are trimethylaluminum, triisobutylaluminum and triethyl-  
 4 aluminum.

5 Preferably the surface modifying agents are the organomag-  
 6 nesium compounds which will have from one to six carbon atoms and most  
 7 preferably  $R^1$  and  $R^2$  are different. Illustrative examples of the  
 8 preferred magnesium compounds are ethyl-n-propylmagnesium, ethyl-n-  
 9 butylmagnesium, amyl-n-hexylmagnesium, n-butyl-sec-butylmagnesium,  
 10 n-butyl-n-octylmagnesium and the like. Mixtures of hydrocarbylmag-  
 11 nesium compounds may be suitably employed such as, for example, di-n-  
 12 butylmagnesium and ethyl-n-butylmagnesium.

13 The magnesium hydrocarbyl compounds are generally obtained  
 14 from commercial sources as mixtures of the magnesium hydrocarbon  
 15 compound with a minor amount of aluminum hydrocarbyl compound. A  
 16 minor amount of aluminum hydrocarbyl is present in order to facilitate  
 17 solubilization and/or reduce the viscosity of the organomagnesium  
 18 compound in hydrocarbon solvent. The hydrocarbon solvent usefully  
 19 employed for the organomagnesium compound can be any of the well known  
 20 hydrocarbon liquids, for example, hexane, heptane, octane, decane,  
 21 dodecane, or mixtures thereof, as well as aromatic hydrocarbons such  
 22 as benzene, toluene, xylene, etc.

23 The organomagnesium complex with a minor amount of aluminum  
 24 alkyl can be represented by the formula  $(R^1MgR^2)_x(R^4Al)_y$  wherein  $R^1$   
 25 and  $R^2$  are defined as above,  $R^4$  is defined as  $R^1$  and  $R^2$  and x is  
 26 greater than 0. The ratio of y over (y+x) is from 0 to less than 1,  
 27 preferably from 0 to about 0.7 and most desirably from about 0 to  
 28 0.1.

29 Illustrative examples of the organomagnesium-organoaluminum  
 30 complexes are  $[(n-C_4H_9)(C_2H_5)Mg][(C_2H_5)_3Al]_{0.02}$ ,  $[(n-C_4H_9)_2Mg]$   
 31  $[(C_2H_5)_3Al]_{0.013}$ ,  $[(n-C_4H_9)_2Mg][(C_2H_5)_3Al]_{2.0}$  and  $[(n-C_6H_{13})_2Mg]$   
 32  $[(C_2H_5)_3Al]_{0.01}$ . A suitable magnesium-aluminum complex is MAGALA<sup>®</sup>,  
 33 BEM manufactured by Texas Alkyls, Inc.

34 The hydrocarbon soluble organomagnesium materials and can be  
 35 prepared by conventional methods. One such method involved, for  
 36 example, the addition of an appropriate aluminum alkyl to a solid  
 37 dialkylmagnesium in the presence of an inert hydrocarbon solvent.  
 38 The organomagnesium-organoaluminum complexes are, for example,

1 described in U.S. Patent No. 3,737,393 and 4,004,071 which are  
2 incorporated herein by reference. However, any other suitable method  
3 for preparation of organometallic compound may be suitably employed.

4 Since, in accordance with this invention, one can produce  
5 high viscosity polymer product at a relatively high temperature,  
6 temperature does not constitute a limiting parameter as with the  
7 prior art homogeneous metallocene/alumoxane catalysts. The catalyst  
8 systems described herein, therefore, are suitable for the polymeri-  
9 zation of olefins in solution, slurry or gas phase polymerizations  
10 and over a wide range of temperatures and pressures. For example,  
11 such temperatures may be in the range of about -60°C to about 280°C  
12 and especially in the range of about 0°C to about 160°C. The  
13 pressures employed in the process of the present invention are those  
14 well known, for example, in the range of about 1 to 500 atmospheres,  
15 however, higher pressures can be employed.

16 The polydispersities (molecular weight distribution)  
17 expressed as Mw/Mn are typically from 2.5 to 100 or greater. The  
18 polymers can contain up to 1.0 chain end unsaturation per molecule.

19 The polymers produced by the process of this present  
20 invention are capable of being fabricated into a wide variety of  
21 articles, as is known for homopolymers of ethylene and copolymers of  
22 ethylene and higher alpha-olefins.

23 In a slurry phase polymerization, the alumoxane cocatalyst  
24 in the alumoxane/aluminum alkyl cocatalyst mixture is preferably  
25 methyl alumoxane and the aluminum alkyl cocatalyst in the mixture is  
26 preferably  $\text{Al}(\text{CH}_3)_3$  or  $\text{Al}(\text{C}_2\text{H}_5)_3$ . The alumoxane and the  
27 aluminum alkyl cocatalyst are dissolved together in a suitable  
28 solvent, typically in an inert hydrocarbon solvent such as toluene,  
29 xylene, and the like in a molar concentration of about  $5 \times 10^{-3} \text{M}$ ;  
30 however, greater or lesser amounts can be used.

31 The present invention is illustrated by the following  
32 examples.

### 33 Examples

34 In the Examples following, the alumoxane employed was  
35 prepared by adding 45.5 grams of ferrous sulfate heptahydrate in 4  
36 equally spaced increments over a 2 hour period to a rapidly stirred 2  
37 liter round-bottom flask containing 1 liter of a 10.0 wt. percent  
38 solution of trimethylaluminum (TMA) in hexane. The flask was main-

1     tained at 50°C and under a nitrogen atmosphere. Methane produce was  
2     continuously vented. Upon completion of the addition of ferrous  
3     sulfate heptahydrate, the flask was continuously stirred and main-  
4     tained at a temperature of 50° for 6 hours. The reaction mixture was  
5     cooled to room temperature and allowed to settle. The clear solution  
6     was separated from the solids by decantation. The aluminum containing  
7     catalyst prepared in accordance with this procedure contains 65 mole  
8     percent of aluminum present as methylalumoxane and 35 mole percent of  
9     aluminum present as trimethylaluminum.

10           Molecular weights were determined on a Water's Associates  
11     Model No. 150C GPC (Gel Permeation Chromatography). The measurements  
12     were obtained by dissolving polymer samples in hot trichlorobenzene  
13     and filtered. The GPC runs are performed at 145°C in trichlorobenzene  
14     at 1.0 ml/min flow using styragel columns from Perkin Elmer, Inc. 300  
15     microliters of a 3.1% solution (300 ml) in trichlorobenzene were  
16     injected and the samples were run in duplicate. The integration  
17     parameters were obtained with a Hewlett-Packard Data Module.

18           Melt index data for the polyethylene products were determined  
19     at 190°C according to ASTM Method D 1238.

#### 20     EXAMPLE 1

##### 21     Catalyst A Preparation

22           10 grams of a high surface area (Davison 952) silica, dehy-  
23     drated in a flow of dry nitrogen at 600°C for 5 hours was slurried  
24     with 50 cc of dry toluene at 30°C under nitrogen in a 250 cc round-  
25     bottom flask using a magnetic stirrer. A solution of 0.200 grams bis-  
26     (cyclopentadienyl) zirconium dichloride and 0.450 grams  $TiCl_4$   
27     dissolved in 25 cc of toluene was added dropwise to the stirred silica  
28     slurry. Stirring was continued for 1 hour while maintaining the  
29     temperature at 30°C, at which time the toluene was decanted off and  
30     the solids recovered. The solid catalyst was washed by stirring and  
31     decantation with three 10 cc portions of toluene and was dried in  
32     vacuum for 4 hours at room temperature. Analysis of the supported  
33     catalyst indicated that it contained 1.1 weight percent titanium and  
34     0.63 weight percent zirconium on the silica.

#### 35     Example 1

##### 36     Gas-Phase Ethylene Polymerization

37           Polymerization was performed in the gas-phase in a 1-liter  
38     autoclave reactor equipped with a paddle stirrer, an external water



1 jacket for temperature control, a septum inlet and a regulated supply  
 2 of dry nitrogen, ethylene, hydrogen and 1-butene. The reactor,  
 3 containing 40.0 grams of ground polystyrene (10 mesh) which was added  
 4 to aid stirring in the gas-phase, was dried and degassed thoroughly at  
 5 85°C. 2.0 cc of a hexane solution of methyl alumoxane and trimethyl  
 6 aluminum which was 0.40 molar in methyl alumoxane and 0.40 molar in  
 7 trimethyl aluminum was injected through the septum inlet, into the  
 8 vessel using a gas-tight syringe. The reactor contents were stirred  
 9 at 120 rpm at 85°C for 1 minute and 0 psig nitrogen pressure. 60.0 mg  
 10 of Catalyst A were injected into the reactor and the reactor was  
 11 pressured to 200 psig with ethylene. The polymerization was continued  
 12 for 10 minutes while maintaining the reaction vessel at 85°C and 200  
 13 psig by constant ethylene flow. The reaction was stopped by rapid  
 14 cooling and venting. 8.7 grams of polyethylene were recovered. The  
 15 polyethylene had a weight average molecular weight of 663,000, a  
 16 number average molecular weight of 5,500, a molecular weight distri-  
 17 bution of 121 and a density of 0.960 g/cc. Specific polymerization  
 18 activity was calculated by dividing the yield of polymer by the total  
 19 weight of transition metal contained in the catalyst by the time in  
 20 hours and by the absolute monomer pressure in atmospheres. For  
 21 example 1, the specific activity is calculated,

$$\begin{aligned}
 \text{specific activity} &= \frac{8.7 \text{ grams}}{.00104 \text{ g Ti + Zr} \times .167 \text{ hr} \times 13.6} \\
 &= 3700 \text{ g/gm} \cdot \text{hr} \cdot \text{atm}
 \end{aligned}$$

## 25 Example 2

### 26 Polymerization

27 Employing Catalyst A, polymerization was performed identi-  
 28 cally as in Example 1 with the exception that 13.0 cc of 1-butene was  
 29 injected after the trimethylaluminum/methylalumoxane solution but  
 30 before the Catalyst A.

31 12.2 grams of polyethylene was recovered. The polyethylene  
 32 had a weight average molecular weight of 333,000, a number average  
 33 molecular weight of 5,700, a molecular weight distribution of 58, and  
 34 a density of 0.920 grams/cc. The specific activity was  
 35 5200 g/g M·hr·atm.

1    Example 32    Polymerization

3            Polymerization was performed with Catalyst A identically as  
4    in Example 1 with the exception that 8.1 mmoles of hydrogen gas were  
5    injected after the trimethylaluminum/methylalumoxane solution, but  
6    prior to the Catalyst A. 10.0 grams of polyethylene was recovered.  
7    The polyethylene had a weight average molecular weight of 516,000, a  
8    number average molecular weight of 4,100, a molecular weight distri-  
9    bution of 126, a density of 0.960 grams/cc. The specific activity was  
10 4300 g/g M<sup>·</sup>hr<sup>·</sup>atm.

11   Example 412   Catalyst B Preparation

13           Catalyst B was prepared identically as Catalyst A with the  
14    exception that 0.500 mg of di(n-butoxy)titanium dichloride was substi-  
15    tuted for the TiCl<sub>4</sub>, and the zirconocene and titanium compound were  
16    dissolved in 10 cc of dry hexane. Analysis of the supported catalyst  
17    indicated that it contained 0.90 weight percent titanium and 0.63  
18    weight percent zirconium.

19   Polymerization (Gas-Phase)

20           The polymerization was performed identically as in Example 3  
21    with the exception that 50.0 milligrams of Catalyst B was substituted  
22    for Catalyst A. 1.4 grams of polyethylene was recovered which had a  
23    weight average molecular weight of 464,000 - a number average mole-  
24    cular weight of 5,900, a molecular weight distribution of 79, and a  
25    density of 0.960 g/cc. The specific activity was 800 g/g M<sup>·</sup>hr<sup>·</sup>atm.

26   Example 5

27           The polymerization was performed identically as in Example 2  
28    with the exception that 50.0 milligrams of Catalyst B was substituted  
29    for Catalyst A. 4.3 grams of polyethylene was recovered which had a  
30    weight average molecular weight of 825,000, a number average molecular  
31    weight of 9,300, a molecular weight distribution of 88, and a density  
32    of 0.928 g/cc. The specific activity was 2,500 g/g M<sup>·</sup>hr<sup>·</sup>atm.

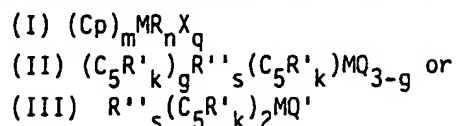
CLAIMS:

1. An olefin polymerization supported catalyst component comprising a support treated with at least one metallocene and at least one non-metallocene transition metal compound.

2. A supported catalyst component according to claim 1 wherein the or each metallocene is of a Group IVB or VB metal of the Periodic Table.

3. The supported catalyst component of claim 2 wherein the metallocene is selected from titanium, zirconium, hafnium or vanadium metallocenes or mixtures thereof.

4. The supported catalyst component of claim 2 or 3 wherein the metallocene is represented by the formula:



wherein Cp is a cyclopentadienyl ring, M is a Group IVB or VB transition metal, X is a halogen, R is a hydride, a hydrocarbyl or hydrocarboxy group having from 1 to 20 carbon atoms, m=1-3, n=0-3, q=0-3 and the sum of m + n + q is sufficient to saturate M, (C<sub>5</sub>R'<sub>k</sub>) is a cyclopentadienyl or a substituted cyclopentadienyl; each R' is the same or different and is hydrogen or a hydrocarbyl radical selected from alkyl, alkenyl, aryl, alkylaryl or arylalkyl radicals containing from 1 to 20 carbon atoms, or two carbon atoms are joined together to form a C<sub>4</sub>-C<sub>6</sub> ring, R'' is a C<sub>1</sub>-C<sub>4</sub> alkylene radical, a dialkyl germanium or silicon or an alkyl phosphine or amine radical bridging two (C<sub>5</sub>R'<sub>k</sub>) rings; Q is a hydrocarbyl radical selected from aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radicals having from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidene radical having from 1 to 20 carbon atoms; s is 0 or 1; g is 0, 1,

or 2; s is 0 when g is 0; k is 4 when s is 1 and k is 5 when s is 0.

5. The supported catalyst component of claim 4 wherein the at least one metallocene is selected from bis(cyclopentadienyl)-zirconium dichloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium methyl chloride, bis(methylcyclopentadienyl)zirconium dimethyl, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium methyl chloride, bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium methyl chloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium dimethyl, bis(methylcyclopentadienyl)titanium diphenyl, bis(methylcyclopentadienyl)titanium dichloride, bis(methylcyclopentadienyl)titanium methyl chloride, bis(methylcyclopentadienyl)titanium dimethyl, bis(pentamethylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl)titanium diphenyl, bis(pentamethylcyclopentadienyl)titanium methyl chloride, bis(pentamethylcyclopentadienyl)titanium dimethyl, bis(n-butylcyclopentadienyl)titanium diphenyl, bis(n-butylcyclopentadienyl)titanium dichloride and mixtures thereof.

6. A supported catalyst component according to any one of the preceding claims wherein the non-metallocene transition metal compound is of a Group IVB, VB or VIB transition metal of the Periodic Table.

7. A supported catalyst component according to claim 6 wherein the non-metallocene transition metal compound is represented by the formula:  $\text{TrX}'_{4-q}(\text{OR}')_q$ ,  $\text{TrX}'_{4-q}\text{R}_q^2$ ,  $\text{VOX}'_3$  or  $\text{VO}(\text{OR}')_3$  wherein Tr is a Group IVB or Group VB metal, Q is 0 or a group, aryl group, or cycloalkyl group having from 1 to 20 carbon

number equal to or less than 4, X' is a halogen, R<sup>1</sup> is an alkyl atoms, and R<sup>2</sup> is an alkyl group, aryl group, aralkyl group, or substituted aralkyl group having from 1 to 20 carbon atoms.

8. The supported catalyst component of claim 7 wherein the non-metallocene transition metal compound is selected from TiCl<sub>4</sub>, TiBr<sub>4</sub>, Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Cl<sub>2</sub>, VCl<sub>4</sub>, VOCl<sub>3</sub>, and ZrCl<sub>4</sub>.

9. A supported catalyst component according to any one of the preceding claims wherein the support is or comprises silica.

10. A supported catalyst component in accordance with any one of the preceding claims wherein the molar ratio of metallocene to non-metallocene transition metal compound is in the range 10:1 to 0.1:1.

11. A supported catalyst component according to any one of the preceding claims which comprises from 0.010 to 2.0 moles of metallocene per gram of support.

12. An olefin polymerization supported catalyst system comprising

- I. a cocatalyst comprising
  - (a) an alumoxane, and
  - (b) an organometallic compound of a metal of Group IA, IIA, IIB, or IIIA of the Periodic Table, and
- II. a supported catalyst component according to any one of the preceding claims.

13. A catalyst system according to claim 12 wherein the molar ratio of alumoxane(s) to metallocene is in the range 1:1 to 100:1.

14. A catalyst system as in claim 12 or 13 wherein the molar ratio of alumoxane (a) to organometallic compound (b) is in the range 10:1 to 0.1:1.

15. A catalyst system according to claim 12, 13 or 14 wherein the organometallic compound (b) is represented by the general formula  $R_nAlX_{3-n}$  wherein R is an alkyl group or an aryl group having from 1 to 18 carbon atoms, X is a halogen atom, an alkoxy group or a hydrogen atom, and n is in the range of 1 to 3.

16. A catalyst system according to any one of claims 12 to 15 wherein the alumoxane is methyl alumoxane.

17. A process for polymering ethylene or copolymerising ethylene with a comonomer selected from alpha-olefins, cyclic olefins, and diolefins, which process comprises polymerizing the (co)monomers in the presence of a catalyst system according to any one of claims 12 to 15.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/02449

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> : C 08 F 10/00; C 08 F 4/60														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding: 5px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC<sup>4</sup></td> <td style="padding: 5px;">C 08 F</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC <sup>4</sup>	C 08 F								
Classification System	Classification Symbols													
IPC <sup>4</sup>	C 08 F													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; padding: 5px;">Category <sup>10</sup></th> <th style="width: 70%; border-bottom: 1px solid black; padding: 5px;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black; padding: 5px;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0128045 (EXXON) 12 December 1984, see claims; page 9, lines 26-31 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4552859 (E.I. BAND et al.) 12 November 1985, see claims --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,12</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4490514 (R.E. HOFF) 25 December 1984, see claim 1  -----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	EP, A, 0128045 (EXXON) 12 December 1984, see claims; page 9, lines 26-31 --	1	A	US, A, 4552859 (E.I. BAND et al.) 12 November 1985, see claims --	1,12	A	US, A, 4490514 (R.E. HOFF) 25 December 1984, see claim 1  -----	1
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>												
A	EP, A, 0128045 (EXXON) 12 December 1984, see claims; page 9, lines 26-31 --	1												
A	US, A, 4552859 (E.I. BAND et al.) 12 November 1985, see claims --	1,12												
A	US, A, 4490514 (R.E. HOFF) 25 December 1984, see claim 1  -----	1												
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<b>IV. CERTIFICATION</b>														
Date of the Actual Completion of the International Search  <div style="text-align: center;">10th February 1987</div>	Date of Mailing of this International Search Report  <div style="text-align: center;">27 MAR 1987</div>													
International Searching Authority  <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="display: flex; align-items: center;"> <div style="margin-right: 10px;">M. VAN MOL</div> </div>													

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/02449 (SA 15406)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/02/87

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0128045	12/12/84	AU-A- 2910984 JP-A- 60035008 US-A- 4530914	13/12/84 22/02/85 23/07/85
US-A- 4552859	12/11/85	None	
US-A- 4490514	25/12/84	EP-A- 0137097 JP-A- 60099106 CA-A- 1216398	17/04/85 03/06/85 06/01/87

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